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Appendix A

Chemical Equilibrium Model Used in Contactor Design Calculations

INTRODUCTION

Determination of the limestone contactor effluent chemistry requires knowledge of the chemical equilibrium conditions in the solution which is immediately adjacent to the limestone surface (see Figure 2 and Eq. 25).

The equilibrium water chemistry at the limestone surface was determined for two cases:

1. When a complete chemical analysis of the raw water is available, and,
2. When only a partial knowledge of the chemical composition of the raw water is available.

Three operational conditions were also considered:

- a. Closed system: The contactor and the contactor effluent are closed to the atmosphere and therefore there is no exchange of carbon dioxide between the solution and the atmosphere.
- b. Open system: The water in the contactor is continuously in equilibrium with atmospheric carbon dioxide.
- c. Closed/Open system: The water in the contactor is closed to the atmosphere but the effluent is open to the atmosphere.

The three operational conditions are illustrated schematically in Figure A.1.

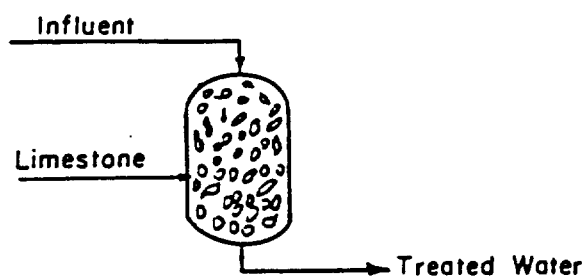
In the description of the computational procedure which follows the knowledge of the raw water chemistry and the operational conditions which pertain to a given procedure are designated by a number and a letter, e.g., "1a" indicates that a complete chemical analysis of the raw water is available and the system is closed to the atmosphere.

The solute species Ca^{++} , H_2CO_3 , $\text{CO}_3^{=}$, H^+ and OH^- in the solution which is immediately adjacent to the limestone particle surface are unknown. To define the solution composition and to determine the unknown species the following equations were used:

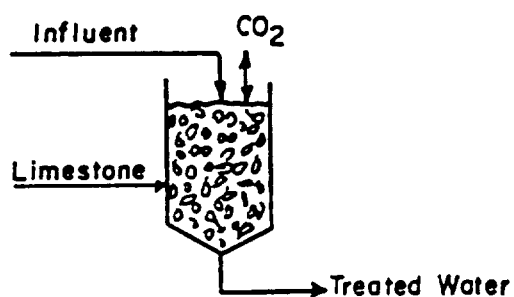
- Charge balance equation:

$$\sum_{i=1}^n Z_i C_i = 0 \quad (\text{A.1})$$

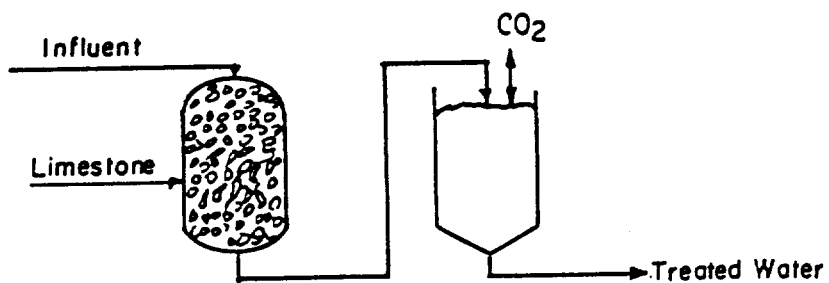
where Z_i and C_i are the charge and molar concentration of specie (i).



(a) CLOSED SYSTEM



(b) OPEN SYSTEM



(c) OPEN/CLOSED SYSTEM

Figure A.1. Operational conditions used in the chemical equilibrium modelling.

- Mass action expressions for the deprotonation of carbonic acid:

$$K_{a1} = \frac{\{H^+\}\{HCO_3^-\}}{\{H_2CO_3\}} \quad (A.2)$$

$$K_{a2} = \frac{\{H^+\}\{CO_3^{2-}\}}{\{HCO_3^-\}} \quad (A.3)$$

where $\{i\}$ is the activity of specie (i).

- Solubility product expression for $CaCO_3(s)$:

$$K_{sp} = \{Ca^{2+}\}\{CO_3^{2-}\} \quad (A.4)$$

- Ion product expression for water:

$$K_W = \{H^+\}\{OH^-\} \quad (A.5)$$

- Henry's law expression for carbon dioxide dissolved in water:

$$K_H = \frac{H_2CO_3^*}{pCO_2} \quad (A.6)$$

where pCO_2 is the partial pressure of carbon dioxide.

- Mass balance equations:

$$DIC = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] \quad (A.7)$$

where

$$[H_2CO_3^*] = DIC \times \alpha_0, \quad (A.8.1)$$

$$[H_2CO_3^-] = DIC \times \alpha_1, \quad (A.8.2)$$

$$[CO_3^{2-}] = DIC \times \alpha_2, \quad (A.8.3)$$

DIC is the dissolved inorganic carbon concentration and α_0 , α_1 and α_2 are the ionization fractions for the carbonate system (Stumm and Morgan, 1981):

$$\alpha_0 = \left(1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2}\right)^{-1} \quad (A.9.1)$$

$$\alpha_1 = \left(1 + \frac{[H^+]}{K_{a1}} + \frac{K_{a2}}{[H^+]}\right)^{-1} \quad (A.9.2)$$

$$\alpha_2 = \left(1 + \frac{[H^+]^2}{K_{a1}K_{a2}} + \frac{[H^+]}{K_{a2}}\right)^{-1} \quad (A.9.3)$$

For a dilute acidic water flowing into the contactor, equation (A.1) becomes:

$$2[\text{Ca}^{2+}] + C_c + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + C_a + [\text{OH}^-] \quad (\text{A.10})$$

where C_c is the total concentration of non-calcium and hydrogen ion cations, in equivalents per liter, C_a is the total concentration of non-inorganic carbon and hydroxyl ion anions in equivalents per liter, and the brackets denote molar concentration.

As water flows through the contactor CaCO_3 is dissolved from the limestone and the calcium and DIC concentrations increase, i.e.,

$$C_{bL} = C_{bo} + S \quad (\text{A.11.1})$$

and

$$\text{DIC} = \text{DIC}_o + S \quad (\text{A.11.2})$$

where C_{bL} and S are the molar concentrations of calcium ion and calcium carbonate dissolved from the limestone at an axial location, L , in the contactor bed, C_{bo} is the calcium concentration in the influent and DIC_o is the influent DIC concentration.

With the substitution of Eqs. (A.8.2), (A.8.3) and (A.11) in the solubility product equation, (A.4), and charge balance equation, (A.10), the following expressions are obtained:

$$2[C_{bo} + S] + C_c [\text{H}^+] = (\text{DIC}_o + S) (\alpha_1 + 2\alpha_2) + C_a + [\text{OH}^-] \quad (\text{A.13})$$

$$\{C_{bo} + S\} \{(\text{DIC}_o + S) \alpha_2\} = K_{sp} \quad (\text{A.14})$$

or

$$S = - \left(\frac{C_{bo} + \text{DIC}_o}{2} \right) + \left(\frac{C_{bo} + \text{DIC}_o}{2} \right)^2 - \left((C_{bo} \times \text{DIC}_o) - \frac{K_{sp}}{\alpha_2 \gamma_2^2} \right)^{\frac{1}{2}} \quad (\text{A.15})$$

where γ_2 is the activity coefficient for divalent ions, in this case the Ca^{2+} and the CO_3^{2-} ions.

Computational Procedure

The equilibrium calculations assume that the influent water is dilute, i.e., the ionic strength, I , is less than 0.01 and negligible complexing of ions occurs.

The equilibrium calcium concentration, C_{eq} , was determined for each set of raw water chemical conditions and temperature using an algorithm in which the pH is systematically varied to find the point at which both the charge

balance, equation (A.13), and the solubility product relationship, equation (A.14) are satisfied.

The search procedure was conducted using three computational loops:

-First loop: the pH interval 6 to 10.5 was searched in steps of 0.25 pH units and the point (pH_1) at which equations (A.13) and (A.14) were satisfied was found.

-Second loop: the pH interval ($\text{pH}_1 \pm 0.30$) was searched in steps of 0.05 pH units and the point (pH_2) at which equations (A.13) and (A.14) were satisfied was found.

-Third loop: the pH interval ($\text{pH}_2 \pm 0.06$) was searched in steps of 0.01 pH units and the point (pH_3) at which equations (A.13) and (A.14) were satisfied was found. At this point:

$$\text{pH}_3 = \text{pH}_{\text{eq}}$$

$$C_{\text{eq}} = C_{\text{bo}} + S \quad (\text{A.16})$$

$$\text{DIC}_{\text{eq}} = \text{DIC}_0 + S$$

In the above calculations the following were considered:

-Equations derived by Plummer and Bussenburg (1982) were used to calculate the equilibrium constants K_{a1} , K_{a2} , and K_H at infinite dilution as a function of temperature. Plummer's equations are given in Table (A.1)..

-The effective CaCO_3 solubility product ($K_{\text{sp}} 20^\circ$) of 1.9×10^{-9} at 20°C (Section 5) was corrected for temperature using the following relationship (Snoeyink and Jenkins, 1980):

$$K_{\text{sp}} = K_{\text{sp}} 20^\circ \left\{ \exp \left[-\frac{H}{R} \left(\frac{1}{T} - \frac{1}{293} \right) \right] \right\} \quad (\text{A.17})$$

where K_{sp} is the CaCO_3 solubility product at temperature, T . Values for the enthalpy, H , and the Boltzmann constant, R , were taken from Snoeyink and Jenkins,

$$\frac{H}{R} = 1484.5 \text{ (degree Kelvin)}$$

Values of the equilibrium constants, K_{a1} , K_{a2} and K_H and the effective CaCO_3 solubility product, K_{sp} , (Equation A.17) for a range of temperature (1 to 25°C) are presented in Table A.2.

Table A-1 Equations Used to Calculate the Equilibrium Constants,
 K_{a1} , K_{a2} and K_H as a Function of Temperature
(Plummer and Bussenburg, 1982)

$$\log K_{a1} = -356.3094 - (0.0609196 \times T) + (2.834.37/T) \\ + (126.8339 \times \log T) - (168491/T^2)$$

$$\log K_{a2} = -107.8871 - (0.03252849 \times T) + (515179/T) \\ + (38.92561 \times \log T) - (563713.9/T^2)$$

$$\log K_H = 108.3865 + (0.0198507 \times T) + (669365/T^2) \\ - (6919.53/T) - (40.45154 \times \log T)$$

where, T, is in degrees Kelvin

-At each pH in the search procedure the ionic strength, I, and the activity coefficients, γ_i , were calculated using

$$I = 1/2(\sum Z_i^2 C_i) \quad (A.18)$$

and

$$\text{Log } \gamma_i = -A Z_i^2 I^{1/2} \quad \text{for } I < 10^{-2.3} \quad (A.19)$$

or

$$\text{Log } \gamma_i = \frac{-A Z_i^2 I^{1/2}}{1 + I^{1/2}} \quad \text{for } I < 10^{-1} \quad (A.20)$$

where $A = 0.509$.

The calculations were made using a computer program written in APL. Outlines of the program calculations are given below for conditions 1a, 1b, 1c, 2a, 2b and 2c.

1.a Closed-to-the-Atmosphere System (Complete Influent Water Chemistry is Known).

After the water chemical composition and temperature are input, the program is used to compute the temperature corrected values of the equilibrium constants K_{a1} and K_{a2} (see Table A.2) and the effective CaCO_3 solubility product K_{sp} (Equation A.17).

-Ionization fractions for the carbonate and bicarbonate ions are then estimated for the first pH value in the interval being searched and the carbonate and bicarbonate concentrations are calculated using equations (A.9.2), (A.9.3), (A.8.2) and (A.8.3).

-The ionic strength, I, is estimated using Eq. A.18 and accordingly the activity coefficients for monovalent, γ_1 , and divalent, γ_2 , ions are calculated using Eq. A.19 or A.20. With the known activity coefficients, the equilibrium constants, K_{a1} and K_{a2} are corrected for ionic strength as follows:

$$K'_{a1} = \frac{K_{a1}}{\gamma_1^2} \quad (A.21)$$

$$K'_{a2} = \frac{K_{a2}}{\gamma_2} \quad (A.22)$$

-New values of the ionization fractions for carbonate and bicarbonate ions are calculated, using the corrected equilibrium constants, K'_{a1} and K'_{a2} (Eqs. A.9.2 and A.9.3). At this point the amount of limestone dissolved, S, is calculated using Eq. A.15 and the value is entered in the charge balance

equation, Eq. A.13. A quantity, DEL, defined as the difference between the left and the right side of the charge balance equation is then calculated:

$$\text{DEL} = \{2[\text{C}_{\text{bO}} + \text{S}] + \text{C}_{\text{c}} + [\text{H}_i^+]\} - \{((\text{DIC}_0 + \text{S})(\alpha_1 + 2\alpha_2)) + \text{C}_{\text{a}} + [\text{OH}_i^-]\} \quad (\text{A.23})$$

-The program then repeats the above calculations using the next pH in the interval. The pH in the search interval at which DEL is a minimum is the point where the solubility product and the charge balance equations (Eqs. A.13 and A.14) are essentially satisfied. In the first loop the pH at the point where DEL is a minimum is pH₁.

After pH₁ is obtained the second loop begins. The calculations in the second and third loop are the same as those in the first loop except, as noted, smaller pH intervals are searched and smaller pH increments are used in the search across each interval.

To use the contactor design equations the calcium concentration in the contactor effluent C_{bL}, must be determined for the case when the effluent is not in equilibrium with the limestone, i.e., pH < pH_{eq} and C_{bL} < C_{eq}. Usually a target effluent pH is known and one must then calculate the corresponding effluent calcium concentration.

The magnitude of C_{bL} for a given effluent pH is determined using the charge balance equation, Eq. A.13. The target effluent pH is used to determine α₁, α₂, [H⁺] and [OH⁻] and these quantities are used with C_{bO}, DIC₀, C_c and C_a to solve Eq. A.13 for the quantity, S. The desired effluent calcium concentration is equal to C_{bO} + S. Note that this value of S is less than the equilibrium value from Eq. A.15.

1.b - Open-to-the-Atmosphere System

For an open to the atmosphere system the computational procedure was the same as that used for a closed-to-the-atmosphere system except that the value of the dissolved inorganic carbon concentration in equations A.13 and A.14 was estimated at each pH using equations A.8.1 and A.6. Combining equations A.8 and A.9 yields,

$$\text{DIC} = \frac{K_{\text{H}} \text{pCO}_2}{\alpha_0} \quad (\text{A.24})$$

Table A-2 Values of K_{a1} , K_{a2} , K_H and $K_{sp}(\text{CaCO}_3)$ for a Range of Temperatures.

The Equations of Plummer and Bussenberg (1982) were used to Calculate these Quantities.

$T^{\circ}\text{C}$	$\log K_{a1}$	$\log K_{a2}$	$\log K_H$	$\log K_{sp}$
1	-6.56	-10.61	-1.12	-8.56
2	-6.55	-10.59	-1.14	-8.57
3	-6.54	-10.58	-1.15	-8.58
4	-6.53	-10.56	-1.17	-8.59
5	-6.51	-10.55	-1.19	-8.60
6	-6.50	-10.54	-1.20	-8.61
7	-6.49	-10.52	-1.22	-8.61
8	-6.48	-10.51	-1.23	-8.62
9	-6.47	-10.50	-1.25	-8.63
10	-6.46	-10.48	-1.26	-8.64
11	-6.45	-10.47	-1.28	-8.65
12	-6.44	-10.46	-1.29	-8.65
13	-6.43	-10.45	-1.31	-8.66
14	-6.42	-10.44	-1.32	-8.67
15	-6.41	-10.42	-1.34	-8.68
16	-6.41	-10.41	-1.35	-8.69
17	-6.40	-10.40	-1.36	-8.69
18	-6.39	-10.39	-1.38	-8.70
19	-6.38	-10.38	-1.39	-8.71
20	-6.38	-10.37	-1.40	-8.72
21	-6.37	-10.36	-1.41	-8.72
22	-6.36	-10.35	-1.43	-8.73
23	-6.36	-10.34	-1.44	-8.74
24	-6.35	-10.33	-1.45	-8.75
25	-6.35	-10.32	-1.46	-8.75

An equation derived by Plummer and Bussenburg (1982) for determining Henry's Law constant for carbon dioxide (see Table A.1) was used with a partial pressure of atmospheric CO₂ of 10^{-3.5}.

1.c - Closed/Open System

The closed/open system calculation involved the pH interval search procedure and Eq. A.23 with the following substitutions;

$$S = 0$$

$$C_{bo} = C_{bL}$$

and from Eq. A.24,

$$DIC_o + S = \frac{K_H pCO_2}{\alpha_o}$$

C_{bL} is the calcium concentration in the contactor effluent. Eq. A.15 is omitted from the pH interval search calculations because the effluent is not in contact with solid CaCO₃.

2 - A procedure for the case when there is limited information on the chemistry of the raw water

The availability of a well equipped laboratory and trained technical personnel in a small water supply system may be limited. In order to proceed with the determination of the chemical equilibrium conditions at the limestone surface, knowledge of the total anion, C_a, and cation, C_c concentrations and their effects on the total ionic strength is necessary to estimate the activity coefficients for individual ions. A procedure was developed for use when only the measured specific conductance, K_m, initial calcium concentration, C_{bo}, initial pH, pH_o, and alkalinity are known.

An equation relating the portion of the total ionic strength contributed by C_c and C_a ions, I_{AB}, to the corresponding specific conductivity, K_{AB}, was derived using data from the analysis of water from 34 lakes in the Adirondack Region of New York State. The equation is given by:

$$I_{AB} = \text{constant} \times K_{AB}. \quad (A.25)$$

The complete chemical analyses for these lakes were obtained from the results of a survey conducted by the U.S. EPA (Kanciruck et al. 1985). The data for the 34 lakes were chosen at random from a list of over 100 lakes.

The MINEQL chemical equilibrium program (Westall et al. 1976) was used to calculate the total ionic strength, I , for each of the 34 sets of data. The total component concentrations and temperature for each lake were entered in the MINEQL program. The values of the ionic strength obtained from MINEQL for the 34 lakes ranged from 2×10^{-4} to 9×10^{-4} M.

The contributions of Ca^{++} , H^+ , OH^- , HCO_3^- , and $\text{CO}_3^{=}$ to the total ionic strength I , was estimated using:

$$I' = 1/2 (4[\text{Ca}^{++}] + [\text{H}^+] + [\text{HCO}_3^-] + 4[\text{CO}_3^{2-}] + [\text{OH}^-]) . \quad (\text{A.26})$$

The ionic strength attributable to C_c and C_a was determined by calculating the difference between the total ionic strength, I , and I' , i.e.,

$$I_{AB} = I - I' . \quad (\text{A.27})$$

The specific conductance attributable to C_a and C_c ions, K_{AB} , was estimated for each lake by computing the difference between the measured specific conductance, K_m , and the sum of the specific conductances attributable to Ca^{++} , H^+ , HCO_3^- , CO_3^{2-} , and OH^- , i.e.,

$$K_{AB} = K_m - K_1 \quad (\text{A.28})$$

where

$$K_1 = [\text{Ca}^{++}] \lambda_{\text{Ca}^{++}} + [\text{H}^+] \lambda_{\text{H}^+} + [\text{HCO}_3^-] \lambda_{\text{HCO}_3^-} + [\text{CO}_3^{2-}] \lambda_{\text{CO}_3} + [\text{OH}^-] \lambda_{\text{OH}^-} \quad (\text{A.29})$$

and, λ , is the specific ionic conductance in water at 25°C , in micromhos/cm.

The values of the specific conductance used in the analysis were taken from Robinson et al. (1959) and are listed in Table A.3. The values of I , K_m , I_{AB} , K_{AB} for the 34 lakes are listed in Table A.4.

TABLE A.3 Individual ion specific conductance

Ion	Specific Conductance, λ
H^+	349.8
HCO_3^-	44.5
$\text{CO}_3^{=}$	69.3
Ca^{++}	59.5
OH^-	198.3

To determine the value of the constant in Equation A.25 a nonlinear least squares procedure which produces least squares or weighted least squares esti-

mates of the parameters of the model was used (SAS 1982). This procedure uses the modified Gauss-Newton iterative method. The analysis gave the following equation:

$$I_{AB} = 1.31 \times 10^{-5} K_{AB} (r^2 = 0.55) \quad (A.30)$$

The low value of R^2 might have resulted from errors in the pH and/or DIC measurements which were used in estimating I_{AB} (see equations A.26 and A.27).

The computational procedure for conditions 2a, 2b and 2c was the same search algorithm as was used for conditions 1a, 1b and 1c. The only difference between the two procedures is in the determination of the ionic strength of the solution at each pH. Determination of the ionic strength of the solution at each pH when limited information is available on the ionic constituents of the raw water can be summarized as follows:

-According to the charge balance equation (A.10):

$$C_{AB} = C_a - C_c = (2[C_{bo}] + [H^+] - (DIC_0(\alpha_1 + 2\alpha_2)) - K_w[OH^-]) \quad (A.31)$$

Since this analysis is intended for use in dilute, low ionic strength systems, it was assumed that the magnitude of C_{AB} is essentially constant during the limestone dissolution process, i.e., its contribution to the total ionic strength of the system is constant and equal to I_{AB} .

The specific conductance attributable to C_a and C_c , K_{AB} , was calculated by combining equations A.28 and A.29, i.e.,

$$K_{AB} = K_m - ([Ca^{++}] \lambda_{Ca^{++}} + [H^+] \lambda_{H^+} + [CO_3^{2-}] \lambda_{CO_3^{2-}} + [HCO_3^-] \lambda_{HCO_3^-} + [OH^-] \lambda_{OH^-}) \quad (A.32)$$

and I_{AB} was calculated using equation A.30.

The contribution to the ionic strength by Ca^{++} , H^+ , OH^- , HCO_3^- , and CO_3^{2-} at each pH was determined by Equation A.18 as follows:

For Condition 2.a,

$$I' = 1/2(4(C_{bo} + S) + [H^+] + ((DIC_0 + S)(\alpha_1 + 4\alpha_2)) + K_w[H]) \quad (A.33)$$

For Condition 2.b,

$$I' = 1/2(4(C_{bo} + S) + [H^+] + (DIC(\alpha_1 + 4\alpha_2)) + K_w[H]) \quad (A.34)$$

where, DIC is estimated using equation A.24.

Table A.4 Ionic Strength and Specific Conductivity for
34 Adirondack Region Lakes

Ref. #	1×10^4 [M]	K_{AB} micromhos/cm	$I_{AB} \times 10^4$ [M]	K_{AB} micromhos/cm
1	3.81	23.70	3.14	16.36
2	1.97	22.70	1.41	13.85
3	4.23	26.00	2.63	19.20
4	2.21	28.00	1.81	17.35
5	2.16	33.70	1.48	17.03
6	2.63	16.60	1.79	13.44
7	2.98	17.60	1.89	13.16
8	3.10	22.40	1.94	18.17
9	2.3	24.50	1.78	15.26
10	2.94	27.10	1.99	17.82
11	3.08	24.10	2.08	18.89
12	3.41	21.00	2.42	16.90
13	2.80	19.90	1.91	15.86
14	4.14	22.60	3.32	16.63
15	6.47	33.40	3.87	20.71
16	7.18	40.40	4.28	26.56
17	7.09	50.50	5.30	43.68
18	6.76	41.10	3.33	23.64
19	7.61	44.00	4.59	39.87
20	8.36	54.80	4.82	38.97
21	6.00	33.40	3.32	20.95
22	6.96	44.90	3.83	30.09
23	8.71	81.30	4.87	63.26
24	5.84	34.80	3.61	25.00
25	5.48	18.00	4.78	13.08
26	4.77	24.10	3.15	16.60
27	2.47	20.90	1.67	16.40
28	2.99	27.00	3.08	18.15
29	5.36	29.00	3.13	19.09
30	4.44	19.06	3.27	14.65
31	4.51	24.20	2.90	17.70
32	4.83	32.80	3.06	24.97
33	6.11	34.20	3.18	21.18
34	7.34	24.7	6.34	14.67

For Condition 2.c,

Equation A.33 was used to calculate the chemistry of the contactor effluent (closed system) and then equation A.34 was used for the condition when the contactor effluent is opened to the atmosphere.

For all conditions, once I_{AB} and I' are known, the total ionic strength of the solution can be estimated using equation A.27,

$$I = I_{AB} + I' \quad (A.35)$$

and the computational procedure for the three conditions (2.a, 2.b and 2.c) proceeds in the same manner as was described for the case when the detailed chemistry (C_a and C_c) is known.

Appendix B
Dissolution Rate Data
from Column Experiments

Run Number	Column ¹	Superficial Velocity (cm/min)	Influent Water Characteristics ²				Overall Dissolution Rate Constant, $K_o \times 10^3$ (cm/min)
			pH	Calcium (mg Ca/L)	Dissolved In- organic Carbon (mg C/L)	Water Tem- perature °C	
1	A	5.5	4.19	0	0.1	16	35
2	A	11.0	4.19	0	0.1	16	54
3	A	16.5	4.19	0	0.1	16	61
4	A	22.0	4.08	0	0.2	16	37
5	A	27.5	4.08	0	0.2	16	54
6	A	5.5	3.92	3.0	0.3	16	37
7	A	11.0	4.00	1.7	0.1	16	22
8	A	16.5	4.00	1.7	0.1	16	44
9	A	22.0	3.92	3.0	0.3	16	51
10	A	27.5	4.00	4.3	0.2	16	62
11	A	27.5	4.34	0.3	0.1	10	46
12	A	41.2	4.50	0	0.1	10	54
13	A	55.0	4.50	0	0.1	10	54
14	A	72.0	4.50	0.3	0.1	10	69
15	A	5.5	4.50	0	0.2	10	18

¹ See Figure for limestone particle diameter and sphericity and bed porosity

² Background electrolyte concentration was 20 mg NaCl/L

Run Number	Column ¹	Superficial Velocity (cm/min)	Influent Water Characteristics ²				Overall Dissolution Rate Constant, $K_o \times 10^3$ (cm/min)
			pH	Calcium (mg Ca/L)	Dissolved Inorganic Carbon (mg C/L)	Water Temperature °C	
16	A	5.5	3.89	3.2	5.5	22	12
17	A	5.5	3.90	5.2	0	22	9
18	A	16.5	3.90	5.2	0	22	22
19	A	5.5	3.91	0.1	0.5	22	55
20	A	16.5	3.91	0.1	0.5	22	82
21	A	27.5	3.91	0.1	0.5	22	101
22	A	27.5	3.89	0.2	1.8	22	64
23	A	16.5	3.89	0.2	1.8	22	49
24	A	5.5	3.89	0.2	1.8	22	23
25	A	54.8	5.45	0	0.3	10	47
26	A	38.4	5.45	0	0.3	10	33
27	A	21.9	5.45	0	0.3	10	16
28	A	5.5	5.45	0	0.3	10	25
29	A	55.0	4.00	0.2	0	10	73
30	A	38.4	4.00	0.2	0	10	52

¹ See Figure for limestone particle diameter and sphericity and bed porosity

² Background electrolyte concentration was 20 mg NaCl/L

Run Number	Column ¹	Superficial Velocity (cm/min)	Influent Water Characteristics ²				Overall Dissolution Rate Constant, $K_o \times 10^3$ (cm/min)
			pH	Calcium (mg Ca/L)	Dissolved Inorganic Carbon (mg C/L)	Water Temperature °C	
31	A	22.0	4.00	0.2	0	10	38
32	A	5.5	4.00	0.2	0	10	32
33	D	8.8	5.99	0.4	0	9	35
34	D	6.1	5.99	0	0	9	15
35	D	3.5	5.48	0	0	9	11
36	D	0.9	5.48	0	0	9	7
37	D	8.8	3.86	0.4	0	9	19
38	D	6.1	3.86	0.4	0	9	17
39	D	3.5	3.88	0.7	0.1	9	11
40	D	0.9	3.98	0.3	0.2	9	6
41	D	8.8	3.41	0.0	0.2	9	21
42	D	6.1	3.41	0.0	0.2	9	18
43	D	3.5	3.56	0.3	0.3	9	20
44	C	54.8	6.12	2.4	0.2	10	105
45	C	38.4	6.12	2.4	0.2	10	52

¹ See Figure for limestone particle diameter and sphericity and bed porosity

² Background electrolyte concentration was 20 mg NaCl/L

Run Number	Column ¹	Superficial Velocity (cm/min)	Influent Water Characteristics ²				Overall Dissolution Rate Constant, $K_o \times 10^3$ (cm/min)
			pH	Calcium (mg Ca/L)	Dissolved Inorganic Carbon (mg C/L)	Water Temperature °C	
46	C	21.9	6.12	2.4	0.2	10	42
47	C	5.5	6.12	2.4	0.2	10	26
48	C	54.8	4.02	0.5	0.2	10	116
49	C	38.4	4.02	0.4	0.2	10	78
50	C	21.9	4.02	0	0.2	10	54
51	C	5.5	4.38	0	0.2	10	23
52	C	54.8	3.53	0.2	0.2	10	63
53	C	38.4	3.53	0.2	0.2	10	40
54	C	21.9	3.53	0.2	0.2	10	27
55	C	5.5	3.53	0.2	0.2	10	12
56	B	54.8	5.45	0	0.3	10	126
57	B	38.4	5.45	0	0.3	10	52
58	B	22.0	5.45	0	0.3	10	25
59	B	5.5	5.45	0	0.3	10	19
60	B	55.0	4.00	0.2	0	10	150

¹ See Figure for limestone particle diameter and sphericity and bed porosity

² Background electrolyte concentration was 20 mg NaCl/L.

Run Number	Column ¹	Superficial Velocity (cm/min)	Influent Water Characteristics ²				Overall Dissolution Rate Constant, $K_o \times 10^3$ (cm/min)
			pH	Calcium (mg Ca/L)	Dissolved Inorganic Carbon (mg C/L)	Water Temperature °C	
61	B	38.4	4.00	0.2	0	10	70
62	B	21.9	4.00	0.2	0	10	45
63	B	5.5	4.00	0.2	0	10	45
64	B	5.5	3.51	0.3	0	10	35

¹ See Figure for limestone particle diameter and sphericity and bed porosity

² Background electrolyte concentration was 20 mg NaCl/L

APPENDIX C

Estimates of Limestone Contactor Cost

The Culligan contactor unit (see Figure 8) with 100 lb (45 kg) of Cullneu medium (2ft^3 (57 L) of medium) costs \$672 installed (March 1986). A 50 lb (23 kg) bag of Cullneu costs \$50.40. Culligan recommends that the unit be used with a flow rate of less than 5 gpm (0.3 L/s) and that the medium be backwashed periodically. The piping supplied with the unit enables one to backwash using the influent flow. Culligan also suggests that the Cullneu medium be replenished by the addition of small amounts ("handfulls") at frequent intervals (monthly).

The box contactor, depicted in Figure 7, was constructed by graduate students at Syracuse University. The materials used in its construction, (plywood, acrylic plastic, fiberglass, etc.) were purchased for approximately \$800. About 80 man-hours of labor were required. The unit contained about 800 lb (363 kg) of limestone. The empty box weighed approximately 400 lbs (182 kg) and therefore installation of the box contactor in the mountain-side spring was a very time-consuming laborious process.

The least expensive approach involves the purchase of a fiberglass pressure vessel and filling it with crushed limestone. This is what was done in the case of the wound-fiberglass column (Column 1, Figure 8). It is recommended that the limestone be analyzed to determine amounts of chemical contaminants and CaCO_3 purity before it is used. The cost of limestone is negligible (\sim \$0.01/lb, \$0.02/kg) compared to the cost of a container. The cost of fiberglass pressure vessels is given in Table C.1. Depending on the size of the unit the cost ranges from \$3 to \$7/L (\$85 to \$198/ ft^3) capacity.

TABLE C.1 Cost of Fiberglass Pressure Vessels

<u>Vessel Volume</u>	<u>Dimensions</u>		<u>Approximate Cost (March 1984)</u>	<u>Approximate Cost Dollars/Liter</u>
	<u>Diameter</u>	<u>Length</u>		
14L	15 cm	46 cm	\$ 92	6.6
28L	20 cm	100 cm	\$137	4.9
57L	20 cm	132 cm	\$198	3.5
100L	33 cm	137 cm	\$296	3.0
142L	36 cm	165 cm	\$410	2.9